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Precise Light-Scattering Studies on Dilute Polymer Solutions II : Low-Angle Light-Scattering Photometer Model LS-1

AUTHOR(S):

Utiyama, Hiroyasu; Sugi, Nagatoshi; Kurata, Michio; Tamura, Mikio

CITATION:

Utiyama, Hiroyasu ...[et al]. Precise Light-Scattering Studies on Dilute Polymer Solutions II : Low-Angle Light-Scattering Photometer Model LS-1. Bulletin of the Institute for Chemical Research, Kyoto University 1969, 46(5): 198-212

ISSUE DATE:

1969-02-15

URL:

<http://hdl.handle.net/2433/76249>

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Precise Light-Scattering Studies on Dilute Polymer Solutions

II. Low-Angle Light-Scattering Photometer Model LS-1¹⁾

Hiroyasu UTIYAMA*, Nagatoshi SUGI²⁾**, Michio KURATA**
and Mikio TAMURA*

Received October 12, 1968

A precise low-angle light-scattering photometer model LS-1 has been constructed by a simple and inexpensive modification applied on the commercial light-scattering photometer PG-21, Shimadzu-Seisakusho Co., Kyoto. No stray light is observed over the angular range 20° – 150° but it amounts to 22% of the scattering from benzene at 12° . No correction for the Fresnel reflection is required and the ratio of the scattering volume at the right angles to the incident light and at an angle θ is strictly $\sin \theta$. The temperature of the liquid under investigation can be kept constant within $\pm 0.02^{\circ}\text{C}$. The measurement of the scattering from benzene at 90 degrees with use of vertically polarized light of wavelength $436\text{ m}\mu$ is possible with the experimental error less than $\pm 0.7\%$.

From the experimental results on the monodisperse poly α -methylstyrene ($\text{MW}=1.87 \times 10^6$) dissolved in benzene at 30.0°C , the following conclusions have been derived. (1) For the precise determination of both the mean square radius of gyration and the second virial coefficient, or even the molecular weight in some cases, the improvement of the experimental accuracy is important as well as the measurement at lower angles. (2) If we plot the square root of the reciprocal scattered intensity function extrapolated to infinite dilution, or to zero scattering angle, the angular dependence or the concentration dependence of the experimental results will be more straightened out than plotting the scattered intensity function itself. But the plotted points show considerable curvature in the plot $\sqrt{Kc/R(\theta)}$ vs. concentration, characteristic of the scattering angle. (3) The particle scattering factor for coil polymers in solution is little affected by the excluded volume effect.

INTRODUCTION

The purpose of the present investigation is to examine the possibility to make a low-angle light-scattering instruments by modifying the light-scattering photometer type PG-21, a product from Shimadzu-Seisakusho Company, Kyoto. The reason we chose type PG-21 is that the instrument is most popular in this country and that we have been using it for a long period of time. The modification should be simple and inexpensive. The modified instrument hopefully embodies such quality that the measurement of the scattered intensity is possible in the angular range between 10° and 150° with the experimental error less than 1% when the reduced scattered intensity is not smaller than $10^{-5}\text{cm}^{-1\ 3)}$. It will be a great success if we keep the experimental error at about 1% even if the reduced

* 内山 敬康, 田村 幹雄: Department of Industrial Chemistry, Kyoto University, Kyoto.

** 杉 長俊, 倉田 道夫: Laboratory of Polymer Solutions, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

scattered intensity is as small as $10^{-6}\text{cm}^{-1\ 4)}$.

After the various important modifications, a new but yet preliminary light-scattering instrument, Model LS-1, has been completed in February, 1968. With this instrument we are able to carry out the light-scattering measurement in the angular range from 17° up to 150° with the desired experimental accuracy. In the present communication we describe the detail of the structure of Model LS-1 and present some important information concerning the procedure to estimate the mean square radius of gyration, based on the results of the light-scattering measurements on the system poly α -methylstyrene-benzene. Please refer to Part I of this series⁵⁾ for the reason why such and such modifications were necessary, because the description is concentrated on the final structure of Model LS-1.

APPARATUS

The Projecting Optical System

The arrangements of the parts of the projecting optical system are illustrated in Fig. 1. A mercury lamp SH200S (Nihon Denchi Co., high pressure, 200 watts) is used as the light source (M_L), as in the commercial light-scattering photometer type PG-21. It is located at a right angle to the direction of the incident beam in order to incorporate a laser in that direction in the later work. The distance

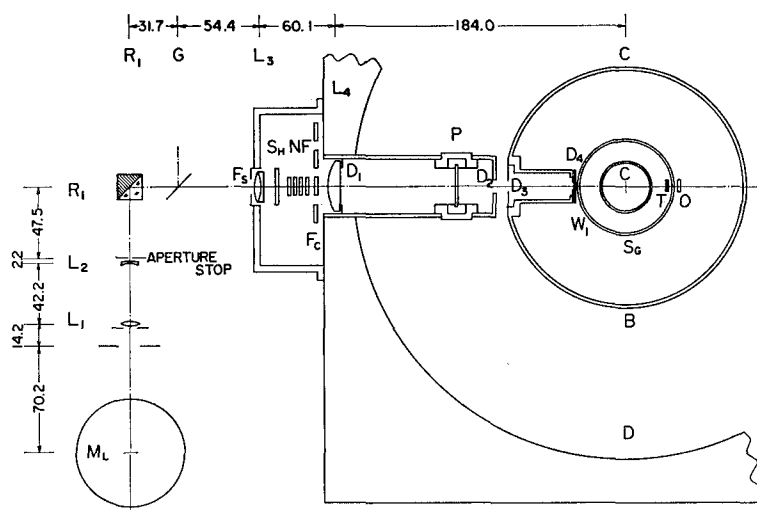


Fig. 1. The arrangement of the parts of the projecting optical system. M_L , high pressure mercury lamp SH200S, 200 Watts, Nihon Denchi Co., Kyoto; L_1 ($f=29.1$, 9^ϕ), L_2 ($f=58.1$, 5^ϕ), L_3 ($f=110.7$, 20^ϕ), L_4 ($f=250$, 37.5^ϕ), lenses; Aperture stop, $1.5(V) \times 0.8(H)$, made with razor blades; R_1 , total reflection prism; G , glass plate of 0.15mm thick to reflect part of the incident light to the monitoring optical system; F_s , field stop, $15(V) \times 10(H)$; S_H , shutter; NF , four neutral filters of transmittance 0.600, 0.350, 0.215, and 0.032; F_C , diffraction colour filter to isolate the mercury lines $436\text{m}\mu$, $546\text{m}\mu$, and $578\text{m}\mu$; D_1 , D_2 , D_3 , D_4 , diaphragms; P , polarizer; W_1 , glass window of 0.15mm thick; C , measuring cell, 44^ϕ ; S_G , removable glass cylinder, 58.7^ϕ , with brass bottom plate; T , glass neutral filter of transmittance 0.01; O , opal diffuser; B , bath made of brass filled with silicon oil, which can be agitated by a motor driven propeller; D , dark room.

between the electric poles is 4.8 mm. The two lenses (L_1 , L_2) function as an achromatic doublet, focusing the image of the mercury arc at the aperture stop. The edges of the aperture stop should be very sharp, and razor blades of stainless steel were found very convenient. The light beam is then reflected to the direction of the incident beam by a total reflection prism (R_1), the orientation of which can be adjusted as shown in Fig. 2.

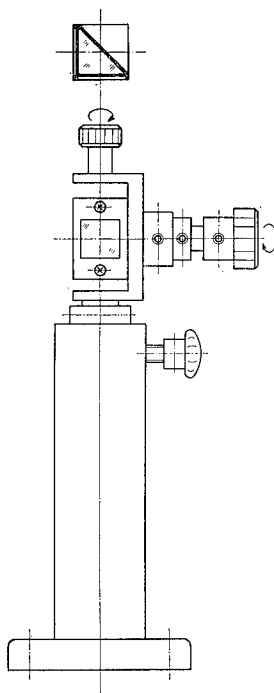


Fig. 2. The total reflection prism fitted with a mechanism of adjusting the orientation around two orthogonal axes.

Another achromatic lens (L_3) is located in type PG-21 at the focal length from the aperture stop. In Model LS-1 we added one more lens (L_4) which, together with the lens (L_3), focuses the image of the aperture stop at the center of the measuring cell. The sizes of the diaphragms (D_1 , D_2 , D_3 , D_4) are made as close as possible to that of the main beam, but the edges never touch the beam.

The size and the position of the aperture stop were so adjusted that only the image of the lower bright spot of the arc near the electric pole of the mercury lamp was formed at the center of the cell, because the hot-spot-jumping was considerable for the upper bright spot. The width of the beam in the cell was 2mm (H) \times 3mm (V). The intensity of the vertical component of the incident light beam is somewhat smaller than that of the horizontal component due to the presence of R_1 and G in the path. The inequality of the components, however, does not affect the accuracy of the measurement because we always take the ratio of the intensity of the scattered light to that of the incident beam.

The intensity of the incident beam is reduced to the level of scattering from pure liquid such as benzene after it passes a pair of glass neutral filter of the

transmittance about 1 % (T) and an opal diffuser (O), both dipped in silicon oil. The amount of the incident beam reflected back into the cell at the interface of the exit surface of the cell and the silicon oil is calculated as 0.345 %. Accordingly about 0.7 % of the incident beam is reflected back before it is absorbed by the neutral filter. We can neglect the effect of this much of reflected light and we need not pay any attention at all to the effect of Fresnel reflection.

The Measuring Cell and the Bath

The largest amount of effort had to be directed to the construction of the bath than any other phase of this work. The detail of the structure of the bath and that of the measuring cell are shown in Fig. 3.

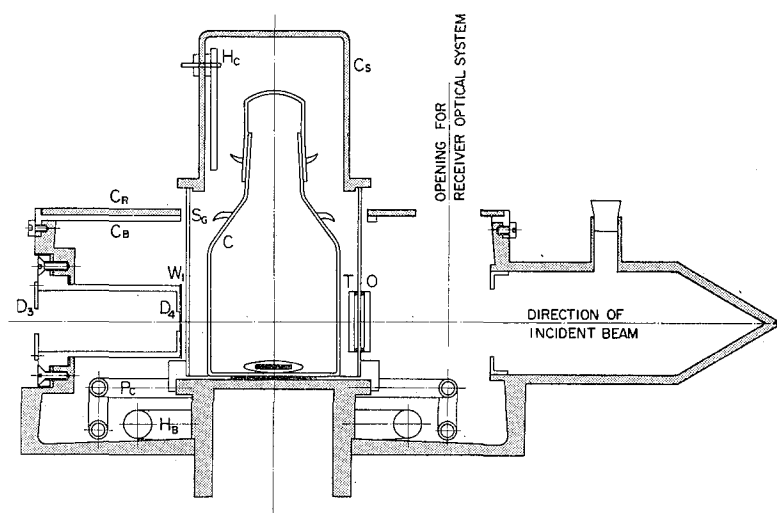


Fig. 3. The detailed structure of the bath B. C, measuring cell with a magnetic stirrer tip in it and a square brass plate ($28 \times 28 \times 1$) attached at the bottom for the accurate and reproducible mounting; C_S , brass cap for the glass cylinder S_G ; H_C , 40 Watts heater, the one generally used in the soldering iron, attached inside the cover C_S to compensate the heat loss from the cover; C_B , brass cover fixed to the bath with an opening for the rotating receiver optical system, C_R , bakelite plate which covers the brass completely and rotates on the brass cover C_B with the motion of the receiver optical system; P_C , pipe for circulating cooling water; H_B , 500 Watts seethe heater.

The measuring cell (C) is an ordinary thin-walled cylindrical vial with a ground glass stopper. The glass material was carefully selected lest it should include any air bubble or scratch. A square 1mm thick brass plate is glued at the bottom of the cell with epoxy resin, which fits exactly to the hollow of the same shape in the bottom plate of the glass cylinder (S_G).⁷⁾ The liquid in the cell (ca. 40ml is necessary) can be agitated by a magnetic stirrer. The cell is positioned accurately and reproducibly at the center of the cylindrical glass container (S_G) with the metal bottom, which is filled with clean silicon oil. It is filtered through a No. 3 glass filter into the glass container each time the cell is introduced for the measurement. The silicon oil⁸⁾ of very low viscosity is extremely useful because the extensive optical purification is not necessary and the epoxy resin is completely stable in it.

Either a glass neutral filter of transmittance 1 % or an opal diffuser is glued by two points with the epoxy resin on both sides of the exit face of the glass container. Inside the cover of brass for the cylindrical glass container (S_G) is attached a small heater (H_O), usually used for the soldering iron, to cover the heat loss from that part of the bath. The cover of the whole bath consists of a brass plate (C_R), fixed to the bath, with a hole in it to accommodate the rotatable receiving optical system, and a bakelite plate (C_B) which covers completely the bath and rotates coaxially with the motion of the receiving optical system.

For the temperature control of silicon oil in the bath, it is equipped with a heater (H_R), a pipe for circulating cooling water in it (P_O), a thermister, and a propeller (not shown) for the agitation. The shaft of the propeller is connected to a small induction motor out of the bath via a universal joint and a ball bearing. Dual voltage is supplied to the heater (H_R) with use of a simple device consisting of a microswitch relay and two slidacs as shown in Fig. 4. Thus the slidac (permanent) is adjusted as high as possible, while the slidac (regulate) supplies slightly higher voltage. The difference must be kept as small as possible to minimize the fluctuation of the temperature. The cooling water is circulated at a constant flow rate in case of need. The temperature of the bath can be controlled constant in this way and with use of a thermistor regulator (Type TR-110, Takara Industrial Company, Minato-Ku, Tokyo) within $\pm 0.02^\circ\text{C}$.

The appropriate voltage must be supplied to the heater (H_O) under the cover to remove the temperature difference between the solution in the cell and the bath.

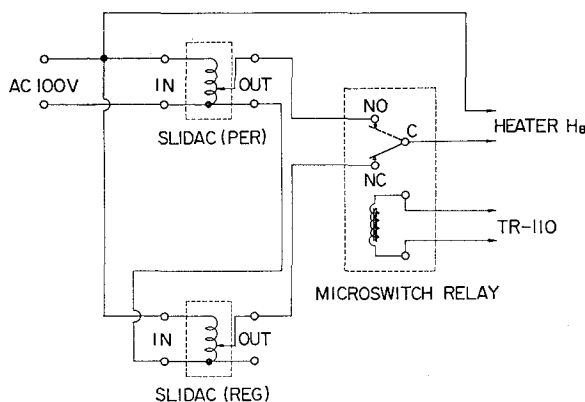


Fig. 4. A simple device for the dual voltage supply to the bath heater H_R . The difference of the voltage supplied by SLIDAC (REG) and SLIDAC (PER) is kept as small as possible to minimize the temperature fluctuation in the bath.

The Receiving Optical System

The receiving optical system is hanged down from a lever arm which rotates coaxially as shown in Fig. 5. The slit system is attached at the bottom of the case for the photomultiplier, and is dipped in the silicon oil in the bath. The slits (S_1 , S_2) must be formed by extremely sharp edges to avoid the stray light to enter into the receiving system. They are both made again with razor blades. By the same reason, the window (W_2), a cover glass for the microscopic observa-

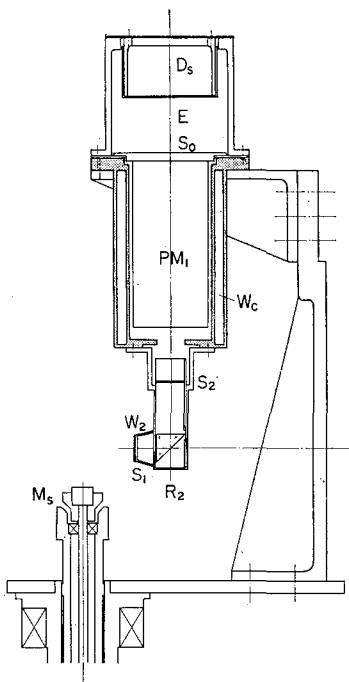


Fig. 5. The receiver optical system. M_s , rotating magnet in the central shaft for stirring liquid in the cell C; S_1 , $3.0(V) \times 0.8(H)$, S_2 , $2.8(H)$, slits made with razor blades; W_2 , glass window of 0.15mm thick; PM_1 , end-on type photomultiplier tube, EMI 6256B, with the observation window 10° ; W_c , water jacket to protect the photomultiplier tube from heat; S_o , socket attached at the bottom of box E for the photomultiplier tube; E, air-tight box for the registers; D_s , container for silica gel to keep the air dry inside the box E. The horizontal distance between the center of the central shaft and that of the photomultiplier tube is 58mm .

tion of the thickness 0.15mm , is completely covered by epoxy resin mixed with carbon black powder except around the edges of the slit (S_1). An end-on type photomultiplier tube type EMI-6256B is fixed to the socket at the bottom of a box (E) which holds in it the wiring system for the photomultiplier tube. A container for silica gel (D_s) is introduced inside the box to remove the moisture. The box is removable from the holder. For the thermal protection of the photomultiplier tube when the working temperature is high, cold water can be circulated through the cavity (W_c) in the case.

The geometry of the receiving optical system is shown in detail in Fig. 6. The dimension of the measuring cell or the distance of the slit (S_1) from the cell center is reduced by a factor of 1.4 considering the refractive index of the silicon oil. The area viewed by the photomultiplier tube in the horizontal direction is defined by the size and position of the slits (S_1 , S_2). The lowest angle we can measure the scattered light without being interfered by the incident beam is determined by the position of the receiving system where it sees the edge of the incident beam at the entrance surface of the cell. It is 9° in the present system. On the other hand, the front slit (S_1) and the size of the viewing window of the photomultiplier tube (10mm°) define the view in the vertical direction.

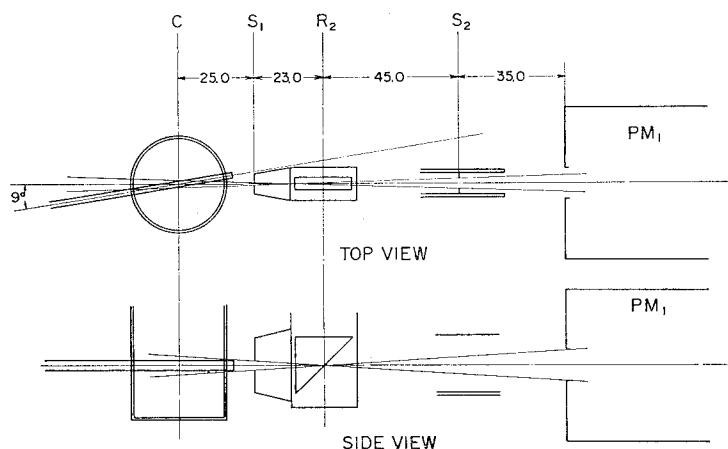


Fig. 6. Geometry of the receiver optical system. The size of the measuring cell and the distance between the center of the cell and the slit S_1 are reduced by a factor of 1.4 because the space is filled with silicon oil. The lowest scattering angle determined by the geometry of the receiver optical system is 9 degrees.

When the measurement of fluorescein is made, an appropriate filter is introduced within the case under the viewing window of the photomultiplier tube.

Both the difference in the sensitivity of the photomultiplier tube and the difference of the reflectivity of the total reflection prism (R_2) to the horizontally and vertically polarized light must be corrected for as the difference in the sensitivity of the receiving optical system to the two directions.

The Monitoring Optical System and the Electronic Design

In the light-scattering photometer LS-1, a very simple monitoring optical system was used as shown in Fig. 7. It consists of very thin glass plate (0.15mm) (G), a combination of a neutral filter and a diffraction color filter (T), an opal diffuser

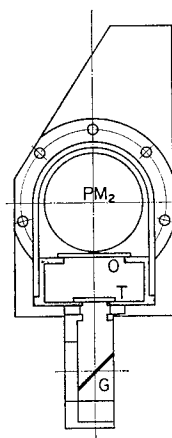


Fig. 7. The monitoring optical system in light-scattering photometer LS-1. G, thin glass plate of 0.15mm thick layed in the incident beam between the total reflection prism R_1 and the field stop F_S ; T, neutral filter of the transmittance 10^{-4} ; O, opal diffuser; PM_2 , monitoring photomultiplier tube R106.

(O), and a photomultiplier tube type RI06 (PM_2). The glass plate (G) is layed in the incident beam between the total reflection prism (R_1) and the field stop (F_s) as shown in Fig. 1.

In the present instrument, essentially the same electronic system for the light-scattering photometer type PG-21 was used together with the ratio recorder type RA-1. They were both purchased from Shimadzu-Seisakusho Co.. The amplification circuit was slightly modified to select the time constant between 0.4 sec to 4 sec.

PERFORMANCE DATA

The Measurement of Fluorescence

In the present instrument the volume viewed at an angle θ by the receiving optical system is equal to the volume viewed at a right angle to the incident beam divided by $\sin\theta$, if the optical systems are aligned correctly. This requirement is confirmed in general by the measurement of the fluorescence at various angles.

Fluorescein was dissolved in cyclohexanol ($n_D^{22}=1.465$) and the solution was filtered through a No. 3 glass filter. The vertically polarized light of the wavelength $436m\mu$ was used for the excitation and an appropriate filter transparent only to the fluorescence was introduced below the measuring photomultiplier tube (PM_1). The experimental results at various angles are normalized as shown in Fig. 8 by plotting $(G_\theta/G_{90}) \sin\theta$ against θ within the deviation $\pm 0.7\%$ in the angular range $12\sim 150^\circ$, where G denotes the recorder deflection. Therefore we conclude that the scattering volume at an angle θ can be normalized simply by multiplying $\sin\theta$ and further volume correction is not necessary.

The Measurement of the Angular Dependence of the Scattering from Benzene

The scattering from benzene was measured at the scattering angles between $12\sim 150$ degrees for the purpose of evaluating the amount of stray light and of calibrating the instrument. The reagent grade benzene (Nakarai Chemical Co., Kyoto) was purified by the repeated shaking first with equal portion of conc. sulfuric acid and then with water and the dilute aqueous solution of sodium hydroxide. It was dried with calcium chloride and distilled in a column over sodium ($n_D^{30}=1.49401$).

The measuring cell was brought to a dust-free condition in an apparatus essentially same as that described by Thurmond.⁹⁾ Benzene was filtered through two sheets of M grade cello filter (Membran Filter Gesellschaft, West Germany) directly into the cell.

The light-scattering measurements were carried out with the vertically polarized light of wavelength $436m\mu$ at $30.0^\circ C$. Then the reduced scattered intensity R_{Uv} (the sum of the vertical and horizontal components of the reduced scattered intensity when the vertically polarized incident beam is used) is constant irrespective of the scattering angle. Therefore the experimental results can be normalized again by plotting $(G_\theta/G_{90}) \sin\theta$.

The result is shown in the upper portion of Fig. 8. It is noted that the stray

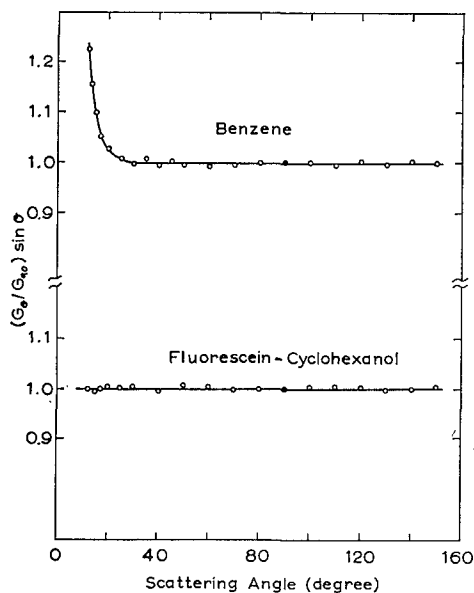


Fig. 8. Angular variation of the scattering from benzene and of fluorescence measured in the light-scattering photometer LS-1 at 30.0°C, with use of vertically polarized light of wavelength $436\text{m}\mu$. In the measurements of fluorescence, very dilute solution of fluorescein in cyclohexanol was used and an appropriate filter was introduced in the receiver optical system to isolate only the fluorescence. The filled circles represent the results at 90 degrees, and G denotes the recorder deflection.

light is absent at angles to as low as 25 degrees, but it begins to appear at lower angles and amounts to 23% of the scattering from benzene at 12 degrees.

If we carry out the light-scattering measurement at a right angles to the incident beam by using both the vertically and horizontally polarized incident light, the depolarization ratio ρ_u can be estimated after the appropriate correction for the difference in the sensitivity of the receiving optical system to the horizontally and vertically polarized light. (see Appendix) The obtained result ($\rho_u=0.426$) is in good agreement with the recently published data.^{10,11)}

Light-Scattering Measurements on Polymer Solutions

The principal purpose of carrying out the light-scattering measurements here on polymer solutions with use of the light-scattering photometer LS-1 is apparently to examine the necessary angular range and the experimental accuracy of the determination of the⁹ reduced scattered intensity enough to obtain the accurate mean-square radius of gyration and the second virial coefficient, or even the molecular weight. The conformation of the macromolecule under consideration is the random coil. Such information is exactly what we need at present because the light-scattering measurements have been restricted heretofore above thirty degrees in general and the experimental error of the determination of the reduced scattered intensity amounts to a couple of per cent. It is a pertinent choice for the present purpose, therefore, that the polymer sample is monodisperse and of largest possible molecular weight, and that the molecule is highly expanded in the

solvent.

The light-scattering experiments were carried out on the system poly α -methylstyrene-benzene. The polymer¹²⁾ was prepared by the anionic polymerization. The sample was purified several times by dissolving it in 2-butanone and reprecipitating by pouring the solution into ethanol, in order to eliminate very small amount of low molecular weight contaminant. The most concentrated polymer solution was prepared by dissolving the well dried polymer sample in purified benzene in a sealed tube and by keeping it overnight at 60°C for the complete solubilization. The solution was centrifuged for the optical purification in a Hitachi preparative centrifuge Type 55 P with use of a fixed angle rotor for ninety minutes at 15000 rpm. It was then transferred carefully into the measuring cell with a dust-free pipet. The concentration of the most concentrated solution was determined by the dry weight method. The measurements on more dilute polymer solution were made by pipetting out a certain amount of solution out of the cell and refilling the cell with dust-free solvent.

The light-scattering measurements were made at 18 scattering angles in the range from 15 degrees up to 150 degrees. Vertically polarized light of wavelength 436m μ was used as the incident beam. Seven polymer solutions covered the concentration from 0.01521 to 0.3800 (g/dl).

The experimental results are illustrated in Fig. 9 as a plot of the reciprocal scattered intensity function $Kc/R(\theta)$ vs. $\sin^2(\theta/2)$. The dotted line is the limiting

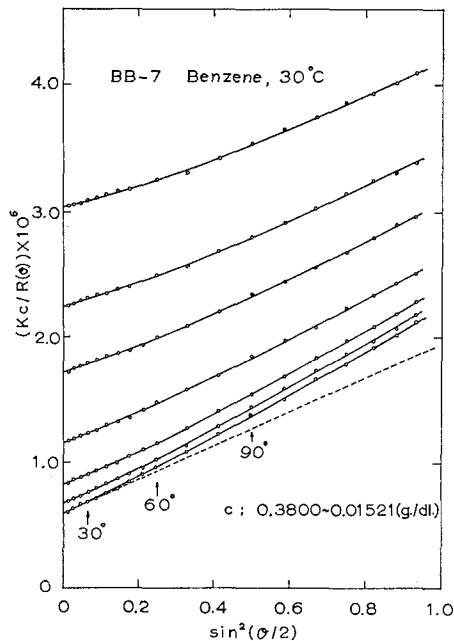


Fig. 9. Angular dependence of the reciprocal scattered intensity function on the system poly α -methylstyrene BB-7 ($MW \approx 1.87 \times 10^6$)—benzene at 30.0°C. Seven samples of the solute concentrations, 0.3800, 0.2808, 0.2067, 0.1213, 0.06020, 0.03153 and 0.01521 (g/dl) were examined. The dotted line indicates the limiting tangent of the plotted points for the lowest solute concentration.

tangent of the plotted points for the smallest solute concentration. At all the scattering angles covered in the present investigation the experimental error of the determination of the Rayleigh ratio is estimated less than $\pm 0.5\%$. It is clearly shown in Fig. 10 that the angular range, where the reciprocal intensity function in the limit of the vanishing concentration exhibits the same angular dependence as the limiting tangent, is restricted, for the present polymer solution, less than about 40 degrees. The concentration dependence of the reciprocal scattered intensity function in the limit that the scattering angle approaches zero also exhibits considerable curvature concave upward.

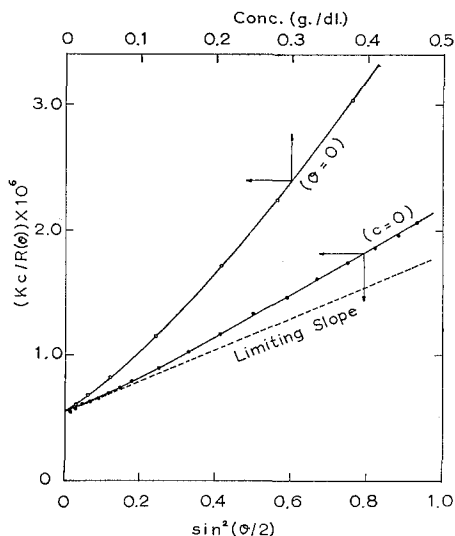


Fig. 10. Concentration dependence of the reciprocal scattered intensity function in the limit that the scattering angle approaches zero (open circles), and the angular dependence of the function extrapolated to infinite dilution (filled circles). The dotted line represents the limiting slope in the latter plot. Experimental data are the same as represented in Fig. 9.

Both curvature can be reduced very much by plotting the square root of the reciprocal intensity function as suggested by Berry.¹³⁾ (Fig. 11) The angular range where the experimental points in the limit that the concentration approaches zero follow the limiting straight line is extended to 60 degrees. It should be emphasized, however, that the extensive curvature still remains when we plot the square root of the reciprocal intensity function for a certain scattering angle against the solute concentration to extrapolate the data to infinite dilution. (see Fig. 12)

It should be kept in mind, therefore, that the square-root-plot only reduces the curvature of the plotted points, being never so effective as to admit the linear extrapolation through the experimental points for all the scattering angles and solute concentrations. Furthermore, it may be concluded that the improvement of the sensitivity and the experimental accuracy is important as well for the precise light-scattering measurements.

If we assume the Rayleigh ratio R_{90} as 49.5×10^{-6} ($436\text{m}\mu$, 30°C) for benzene¹¹⁾ and (dn/dc) for the present system is $0.130_6^{19)}$, we obtain the results

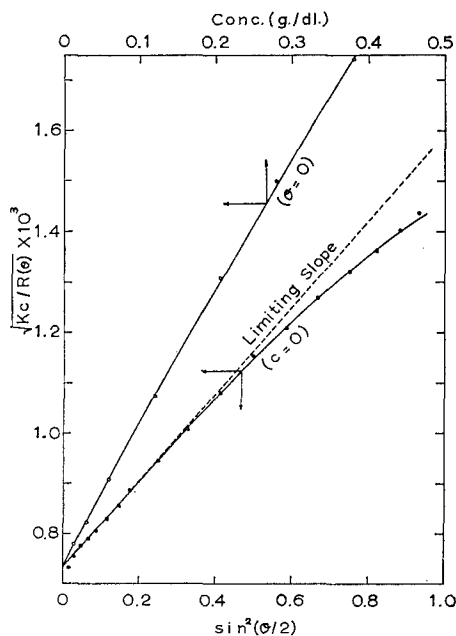


Fig. 11. Plot of the square root of the reciprocal scattered intensity function in the limit that the scattering angle approaches zero vs. the solute concentration (open circles), and the plot of the same function at infinite dilution vs. $\sin^2 (\theta/2)$ (closed circles). The dotted line represents the limiting slope in the latter plot.

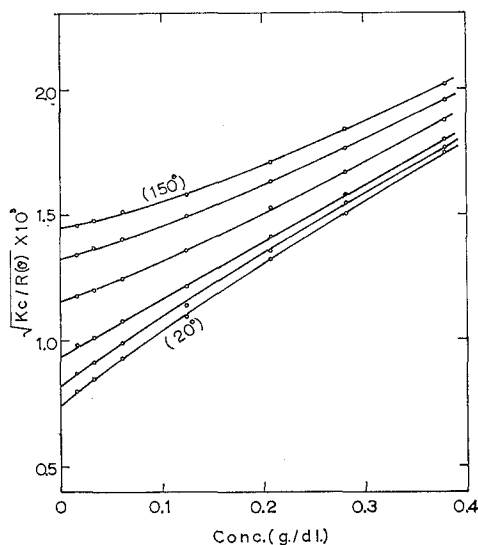


Fig. 12. Concentration dependence of the square root of the reciprocal scattered intensity function for the scattering angles 20° , 40° , 60° , 90° , 120° , and 150° . The experimental data are the same as represented in Fig. 9.

$MW=1.87 \times 10^6$, $A_2=2.16 \times 10^{-4}$, and $\langle S^2 \rangle^{1/2}=619 \text{ \AA}$.

DISCUSSION

Here we consider the problem to estimate the mean square gyration radius from the light-scattering experimental results which are restricted above a certain scattering angle. The experimental error of the determination of the reciprocal scattered intensity function is assumed negligible.

If the correct closed form of the particle scattering factor $P(\theta)$ for the polymeric solute is not available, the only way of determining the gyration radius is obviously to estimate the limiting slope in the plot of the reciprocal intensity function extrapolated to infinite dilution vs. $\sin^2 (\theta/2)$. The accuracy of the estimated gyration radius depends solely on how small is the parameter x , defined below, for the lowest scattering angle.

$$x = (4\pi^2 n_0 / \lambda_0)^2 \langle S^2 \rangle \sin^2 (\theta/2) \quad (1)$$

Unfortunately, however, the parameter x cannot be evaluated before the gyration radius is determined unambiguously from the light-scattering measurements carried out at small enough scattering angles. The determination of the gyration radius or even the molecular weight or the second virial coefficient of high molecular weight DNA provides a typical example of such circumstance.^{6,14)}

For the coiling polymer solute, we are permitted to make use of the particle scattering factor for the gaussian chain for monodisperse ideal solutions,¹⁵⁾ which reads¹⁶⁾

$$P(x) = (2/x^2) (e^{-x} - 1 + x) \quad (2)$$

The residual effect we have to consider is the molecular weight distribution and the nonideality. As long as we use a sample which is produced by the anionic polymerization and is subject to a purification procedure to remove the low molecular weight contaminant, the sample may be considered as monodisperse. The nonideality effect on $P(\theta)$ may then be examined by comparing the experimental results on BB-7 in benzene with the above expression.

To our surprise, the reciprocal scattered intensity function extrapolated to infinite dilution stands in perfect agreement with Eq (2) when the argument x is calculated with use of the gyration radius determined from the limiting tangent. It is apparently necessary to accumulate the experimental results before the final conclusion is drawn, but we briefly mention the importance the present observation infers.

Since the particle scattering factor is available at hand in a closed form, the experimental results at high scattering angles are useful, as well as the results at low scattering angles, to determine the gyration radius provided that the experimental accuracy is sufficiently high. Therefore the present observation provides an experimental support to the classical dissymmetry method,¹⁷⁾ although the method is apparently too simplified for the accurate measurements.

Finally we have to stress that the improvement of the light-scattering photometer is undertaken solely to obtain more accurate molecular weight, more accurate second virial coefficient, and more accurate mean square radius of gyration. Effort should not be directed to the determination of the number average mole-

cular weight, for example, on a polydisperse polymer sample.¹⁸⁾ Such information does not deserve the difficulty to extrapolate the scattered intensity function at infinite dilution to large value of x , not of $\sin^2 (\theta/2)$.

APPENDIX

We consider the scattering from pure liquid at a right angle to the incident beam. The four components of the Rayleigh ratio R are represented by

$$\left. \begin{aligned} (G_{90}/G_0)_{Vv}\phi_{Vv} &= R_{Vv} & (G_{90}/G_0)_{Hv}\phi_{Hv} &= R_{Hv} \\ (G_{90}/G_0)_{Vh}\phi_{Vh} &= R_{Vh} & (G_{90}/G_0)_{Hh}\phi_{Hh} &= R_{Hh} \end{aligned} \right\} \quad (3)$$

where G_0 and G_{90} represent the recorder deflection when the receiver optical system is in the direction of the incident beam and at a right angle to the beam, respectively, and ϕ denotes the calibrating constant. The suffix Vh , for example, represents the experimental condition that the axis of a hypothetical analyzer at the slit S_1 is in the vertical direction, whereas that of the polarizer is in the horizontal direction.

Since the incident beam is completely depolarized after it passes the opal diffuser O , the following equations hold.

$$\phi_{Vv} = \phi_{Vh}, \quad \phi_{Hv} = \phi_{Hh} \quad (4)$$

Denoting the ratio of the sensitivity of the receiver optical system to the horizontally and vertically polarized light as k , we obtain

$$k\phi_{Hv} = k\phi_{Hh} = \phi_{Vv} = \phi_{Vh} \equiv \phi \quad (5)$$

Therefore the ratio of the recorder deflection $(G_{90}/G_0)_v$ when the vertically polarized incident light is used, or $(G_{90}/G_0)_h$ reads

$$(G_{90}/G_0)_v = (G_{90}/G_0)_{Vv} + (G_{90}/G_0)_{Hv} = \phi^{-1}(R_{Vv} + R_{Hv}) \quad (6)$$

$$(G_{90}/G_0)_h = (G_{90}/G_0)_{Vh} + (G_{90}/G_0)_{Hh} = \phi^{-1}(R_{Vh} + R_{Hh}) \quad (7)$$

For pure liquids, the four components of the Rayleigh ratio are mutually related by the following equations,

$$\left. \begin{aligned} R_{Hv} &= R_{Vh} = R_{Hh} = \left(\frac{\rho_u}{1 + \rho_u} \right) R_u \\ R_{Vv} &= \left(\frac{2 - \rho_u}{1 + \rho_u} \right) R_u \end{aligned} \right\} \quad (8)$$

where ρ_u denotes the depolarization ratio and R_u the Rayleigh ratio when neither polarizer nor analyzer is used. Using the above relations in Eqs (6), (7), we get the necessary equations as

$$\left. \begin{aligned} (G_{90}/G_0)_v &= \phi^{-1} \frac{2 - (1 - k)\rho_u}{1 + \rho_u} R_u \\ (G_{90}/G_0)_h &= \phi^{-1} \frac{(1 + k)\rho_u}{1 + \rho_u} R_u \end{aligned} \right\} \quad (9)$$

The depolarization ratio ρ_u is determined using the experimental quantity ρ' ($= (G_{90}/G_0)_h / (G_{90}/G_0)_v$) as

$$\rho_u = \frac{2\rho'}{(1+k) + (1-k)\rho'} \quad (10)$$

In the present instrument, k is 1.118 (436m μ).

ACKNOWLEDGEMENTS

We would like to express our sincere thanks to Mr. Toichiro Ueda and Mr. Kichizo Ohno of the machine shop of this Institute for the mechanical works and the advice. The present investigation will not have been brought to completion without their help. Some technical assistance of Mr. Yoshisuke Tsunashima of our group in the later part of this job is appreciated. The grant-in-aid from the Ministry of Education (Shiken Kenkyu, 1964-1965) is gratefully acknowledged.

REFERENCES

- (1) Taken in part from thesis submitted by N. S. in partial fulfilment of the requirements for the master's degree. Department of Industrial Chemistry, Kyoto University, 1968. An account of this paper will be presented at the 17th Polymer Symposium of Japan to be held at Ehime University, October, 1968.
- (2) Present Address, The Central Research Institute, Japan Geon Company, Kawasaki-shi, Kanagawa, Japan.
- (3) The V_h component of the scattering from benzene, or the U_u component of the scattering from carbon tetrachloride are about that order of magnitude for the incident beam of the wavelength 436m μ .
- (4) The V_h component of the scattering from carbon tetrachloride is 0.752×10^{-5} for the incident beam of the wavelength 436m μ .
- (5) H. Utiyama, N. Sugi, M. Kurata, and M. Tamura, "Precise Light-Scattering Studies on Dilute Polymer Solutions. I. Discussion of the Light-Scattering Photometers," *This Journal* Vol. 46, pp 77-86 (1968).
It is our regret that very important low-angle light-scattering apparatus designed by Froelich *et al.*⁶ has been dropped out of consideration in Part I.
- (6) D. Froelich, C. Strazielle, G. Bernardi, and H. Benoit, *Biophys. J.*, **3**, 115 (1963).
- (7) The price of a measuring cell is 1500 Yen, available from Kitamura Seisaku-Sho, Naga-hama-shi, Shiga. We are using 25 measuring cells.
- (8) A commercial product from Shinetsu Chemical Industry, Tokyo, Type KF-96. The viscosity is about 10 c. s. at room temperature and $n_D^{25} = 1.400$.
- (9) C. D. Thurmond, *J. Polymer Sci.*, **8**, 607 (1952).
- (10) R. C. C. Leite, R. S. Moore, and S. P. S. Porto, *J. Chem. Phys.*, **40**, 3741 (1964).
- (11) D. J. Coumou, *J. Colloid Science*, **15**, 408 (1960).
- (12) The sample was a generous gift from Mr. Kuniaki Sakato of our group and designated as BB-7. The molecular weight of the sample estimated from the reaction kinetics was 2.0×10^6 .
- (13) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).
- (14) J. A. Harpst, A. L. Krasna, and B. H. Zimm, *Biopolymers*, **6**, 595 (1968).
- (15) P. J. Flory and R. L. Jernigan, *J. Am. Chem. Soc.*, **90**, 3128 (1968).
- (16) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).
- (17) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).
- (18) G. Meyerhoff, U. Moritz, and R. L. Darskus, *Polymer Letters*, **6**, 207 (1968).
- (19) K. Sakato, private communication.